Characterization of air/water interface adsorption of a series of partially fluorinated/hydrogenated quaternary ammonium salts

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A B S T R A C T

The adsorption at air/water interface of a series of partially fluorinated/hydrogenated quaternary ammonium salts was characterized by the determination of static and dynamic surface tension, critical micelle concentration, surface excess, area per molecule and Krafft temperature. In particular, the variation of these parameters was studied as a function of fluorinated and hydrogenated chain length.

Modification of fluorinated and hydrogenated moieties allows to finely tune all the aforementioned physical surface properties: increasing the number of fluorinated carbon atoms boosts both effectiveness and efficiency of surfactant in reducing surface tension, kinetics of migration to interface are favored fastening reaching of equilibrium conditions, critical micelle concentration is reduced and surface excess is increased. Conversely increasing the length of the hydrogenated moiety reduces both effectiveness and efficiency of surfactant, migration to interface is slackened, c.m.c. is increased, and surface excess is depresses. Area per molecule and Krafft temperature appear to be affected mainly by the total number of carbon atoms introduced in the molecules whatever the nature of the substituent (fluorine or hydrogen).

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1. Introduction

Surfactants are among the most versatile products of the chemical industry, appearing in several industrial applications such as motor oils [1], pharmaceutics [2], detergents [3], petroleum recovery [4], electronic printing, magnetic recording or biotechnology [5]. Cationic surfactants dissociate in water, forming surface-active positively charged ions and negatively charged counter-ions. The introduction of fluorinated chains in cationic surfactants is very promising because of their strong surface activity, high hydrophobicity and molecular stiffness which cause the formation of aggregates with little curvature [6]. One special type of fluorinated cationic surfactants are mixed quaternary ammonium compounds which have a fluorinated hydrophobic/ lipophobic moiety and a hydrocarbon hydrophobic/lipophilic moiety bonded to a hydrophilic quaternary ammonium group. By varying the length of different segments the hydrophobic– lipophobic–lipophilic character of surfactants can be modified allowing to finely tune physico/chemical properties such as surface and interface tension. While an increased hydrophobic character

(obtained by lengthening hydrocarbon moieties) plays a favorable role in antibacterial applications [7,8], a stronger hydrophobic/ lipophobic character (obtained by lengthening the fluorocarbon chain) causes in the formation of an insulating thin aqueous film on hydrocarbon fuels during fire-fighting foam flow [9].

In a previous paper [10], we showed that surfactants with long fluorinated chains and relatively short hydrocarbon chain can form long and highly flexible aggregates leading to highly viscous solutions and the formation of an entangled network made of flexible worm-like micelles. These particular micellar aggregates are due to weak non-covalent interactions which facilitate an easy and fast change in their structure in response to external actions.

The aim of this study is to examine how the chemical structure of surfactant, that is the length of fluorinated and hydrocarbon chains, influences interfacial properties.

The characterization of adsorption phenomena at air/water interface of partially fluorinated/hydrogenated ammonium quaternary surfactants was achieved determining key parameters such as parameters such as critical micelle concentration, superficial tension, surface excess, area per molecule, Krafft's temperature and dynamic surface tension allowed the subsequent characterization of adsorption phenomena of fluorinated quaternary surfactants at air/water interface.

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2. Experimental

2.1. Materials and methods

All dialkyl ammine [alkyl = methyl, ethyl, propyl, butyl, hexyl, octyl] and solvents were purchased from Aldrich and used without further purification. 3-Perfluorobutyl-1,2-epoxypropane, 3-perfluorohexyl-1,2-epoxypropane, and 3-perfluorooctyl-1,2-epoxypropanewere synthesized according to the previously reported procedure [10].

2.2. Surface tension(γ), surface excess (Γ), area per molecule at critical micelle concentration ($A_{c.m.c.}$)

Surface tension of aqueous solutions of partially fluorinated surfactants were measured using a Kruss K100 tensiometer by the Wilhelmy plate technique which allowed to plot surface tension as a function of time (in order to follow adsorption kinetics) till equilibrium. Partially fluorinated quaternary ammonium compounds which were sparingly soluble in water were dissolved in a 10% methanol aqueous solution [11] and measurements were performed at 25 °C.

Determination of critical micelle concentration (c.m.c.) was carried out by adding a concentrated surfactant solution to water and measuring surface tension at each addition. Surface excess concentration (Γ) was determined by the slope of surface tension curves as a function of concentration. Surface excess concentration at surface saturation Γ_m is a useful measure of the effectiveness of adsorption of the surfactant at the liquid/air or liquid/liquid interface, since it is the maximum value that adsorption can attain. The adsorption effectiveness is a key factor in determining surfactant properties such as foaming, wetting and emulsification. Tightly packed, coherent interfacial films display very different interfacial properties compared to loosely packed, non coherent films. Hydrophobic chains of surfactants adsorbed at the water–air or water-hydrocarbon interfaces do not display a close-packed arrangement normal to the interface at saturation adsorption.

The adsorbed amount of a surfactant (Γ) can be calculated according to the Gibbs adsorption [12]:

$$\Gamma = -\frac{1}{4.606\,RT}\left(\frac{d\gamma}{d\log_{10}C}\right)_T \tag{1}$$

For surfactants with a single hydrophilic group, either ionic or nonionic, the area occupied by a molecule at the surface is determined by the hydrated hydrophilic group rather than by the hydrophobic group. The area occupied by a surfactant molecule ($A_{c.m.c.}$) at the air/water interface (expressed in square angstroms) is derived from the value of adsorbed amount of surfactant at the c.m.c. ($\Gamma_{c.m.c.}$) by using the following expression:

$$A_{c.m.c.} = \frac{1}{N\Gamma_{c.m.c.}} \tag{2}$$

where N is Avogadro's number. A decrease in the area occupied by a surfactant molecule indicates a greater effectiveness of adsorption.

Specific interfacial area per molecule at c.m.c. ($A_{c.m.c.}$) provides information on the degree of packing and orientation of the adsorbed surfactant molecule and these data are in agreement with molecule dimensions obtained by molecular models.

2.3. Dynamic surface tension

Dynamic surface tension (DST) data have been obtained by the maximum bubble pressure method using a SITA pro line t15 instrument. DST measurements were performed with effective surface ages ranging from 10 ms to 20 sand at a concentration twelve times the c.m.c. using a capillary terminating with an open end below the free surface of a liquid. The test gas is then let flow into the pipe, while its pressure is constantly monitored. First, a curved gas/liquid interface forms inside the tube, which is then driven down the capillary by the gas flow. The pressure rises until a hemisphere is formed at the tip of the capillary. The value of pressure measured in this moment (maximum pressure) is directly proportional to the surface tension at the time when the hemisphere is formed. If p_0 is the hydrostatic pressure at the tip of the capillary, R is the maximum bubble radius and p_{max} is the maximum value of the pressure, the DST at the time when p_{max} is reached is derived via Laplace's relation:

$$\sigma_{t\,max} = \frac{p_{max} - p_0}{2}R \tag{3}$$

Once reached the maximum value, the pressure starts to drop as the bubble size keeps increasing, until the bubble will eventually drop off the tube and migrate to the surface. At that point, another bubble will start to form and the process will repeat. By tuning the frequency of bubbles the DST at different times can be monitored.

2.4. Krafft temperature

Aqueous solutions were prepared at concentration double than the c.m.c. and kept at 5 °C for 24 h, where precipitation of surfactant hydrated crystals occurred. The temperature of the precipitated system was then raised [13] and conductivity variation measured.

2.5. Synthesis general procedures

Partially fluorinated/hydrogenated tertiary symmetric ammines having n fluorinated carbon atoms and m hydrogenated carbon atoms (A_{nm}) and partially fluorinated/hydrogenated quaternary surfactants (F_nH_m) were prepared according to the procedure previously reported [14]. The schematic structure of synthesized surfactants is summarized in Scheme 1.

2.6. Characterization

Intermediates tertiary amines (A_{nm}) and desired surfactants (F_nH_m) were characterized by nuclear magnetic resonance (NMR) (Bruker W-200 MHz instrument) and mass spectrometry (MS) (Thermo TRACE GC instrument from Thermo Fischer 81 Corp. fitted with an Automass III Multi spectrometer (electron ionization at 70 eV).

2.6.1. Characterization of partially fluorinated/hydrogenated tertiary amines (A_{nm})

1-Dimethylamino-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11 heptadecafluoro undecan-2-ol (A_{81})

MS m/z (rel. ab. %): 521 ([M]$^{+\bullet}$, 5%); 506 ([M − CH$_3$]$^+$, 20%), 88 ([M − CF$_3$(CF$_2$)$_7$, −CH$_2$]$^+$, 10%), 58 ([M − CF$_3$(CF$_2$)$_8$CHOHCH$_2$]$^+$, 100%);

^{1}H NMR (CD$_3$OD): δ = 2.39 (m, CH$_2$(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH$_2$(c), 2H); 2.29 (t, CH$_3$(d), 6H); 4.2 (d, OH(e), 1H).

^{19}F NMR (CD$_3$OD): δ = −80.9 (t, CF$_3$(a), 3F); −111.7 (m, CF$_2$CH$_2$(b), 2F); −126.2 (m, CF$_2$(c), 2F); −123.3 (m, CF$_2$(d), 2F); −122.8 (m, CF$_2$(e), 2F); −121.9 (m, CF$_2$(f), 2F); −121.6 (m, CF$_2$(g,h), 4F).

1-Diethylamino-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11 heptadecafluoro undecan-2-ol (A_{82})

MS m/z (rel. ab. %): 549 ([M]$^{+\bullet}$, 3%), 116 ([M − CF$_3$(CF$_2$)$_7$, −CH$_2$]$^+$, 30%), 86 ([M − CF$_3$(CF$_2$)$_8$CHOHCH$_2$]$^+$, 100%, 69 [CF$_3$]$^+$ 15%;

^{1}**H NMR** (CD$_3$OD): δ = 2.18 (m, CH$_2$(a), 1H); 2.49 (m, CH$_2$(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH$_2$ (c,d,), 6H); 1.04 (t, CH$_3$(e), 6H); 4.1 (d-d,OH(f), 1H).